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NONSTOICHIOMETRY AND PROBLEMS OF PREVENTION OF POLYMORPHIC TRANSFORMATIONS IN CRYSTALLINE COMPOUNDS

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Translated from *Steklo i Keramika*, No. 11, pp. 20 – 24, November, 1999.

The effect of defects of the tungsten trioxide crystal lattice caused by disturbance of the stoichiometry on the polymorphic transformations arising as a consequence of temperature variations is considered. It is demonstrated that the introduction of a more electropositive metal in tungsten trioxide, which transforms this oxide into tungsten oxide bronze, suppresses the phenomenon of nonstoichiometry in oxygen, which creates conditions for stabilization of the polymorphic modifications in a wide temperature range.

Oxide bronzes are ternary chemical compounds of the type M_xMeO_n (M and Me are metallic components), where the electronegativity of Me (usually a d -element of groups IV – VIII of the periodic system of elements) is always higher than the electronegativity of M (usually alkaline or alkaline-earth elements). The matrix structural base in these compounds consists of MeO_n oxides linked in bonded oxygen octahedrons, inside which the more electronegative metal Me is positioned. There are extensive published data on tungsten-lithium, tungsten-sodium, tungsten-potassium, and tungsten-rubidium oxide bronzes; oxide-vanadium and other bronzes have been studied in detail as well [1 – 7].

The nonstoichiometry of oxide bronzes has certain specifics, which we will consider using the well-studied oxide-tungsten bronze as an example.

Tungsten trioxide crystals, the same as rhenium trioxide crystals, are constructed from octahedrons bonded by their apexes occupied by oxygen. Tungsten is localized inside the octahedrons. With such type of polyhedral linking, tungsten forms a cubic cation sublattice, and vacancies inevitably arise in the crystal. These vacancies in a cubic structure are octahedric as well, and their quantity is equal to the quantity of the lattice points formed by tungsten (Fig. 1, right). These voids can be occupied by another metal.

Such crystal formations in the literature are known as “implantation (inclusion) structures,” in which the matrix formed by polyhedrons is a “host” capable of receiving a “guest” [8]. Such structures include oxides bronzes, where the oxide of the more electronegative metal is the host and the more electropositive element is the guest. The properties of oxide bronze are determined by the concentration of this

element and the change when the latter varies. The value of x in the formula M_xMeO_n should vary from zero to unity. The state with $x = 1$ is typical of perovskite (Fig. 1, left). The parameter x never attains its maximum value in bronzes. The reason is that some of the vacancies emerging in the formation of the WO_3 lattice are occupied by excessive tungsten that is accumulated in the crystal when the stoichiometry in this oxide is disturbed. That is why all bronzes are always nonstoichiometric with respect to the more electropositive cation.

The nonstoichiometry of oxide bronzes, in particular, their homogeneity fields are described using the parameter of the concentration of the more electropositive incorporated metal. Variation of the parameter x is associated with the modification of the nonstoichiometric phase.

The simplest method for the production of sodium-tungsten bronze is exposure of tungsten trioxide in sodium vapor, whose atoms penetrate into WO_3 and gradually fill the vacancies in its crystals.

If WO_3 has a cubic lattice, sodium atoms find themselves surrounded by six oxygen atoms, whose chemical bond with tungsten atoms has a substantial share of covalence. Since

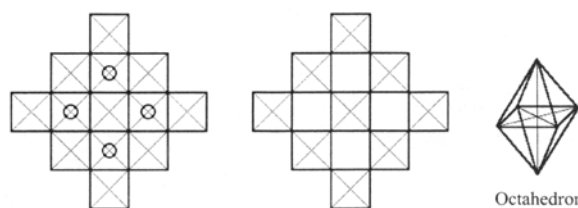


Fig. 1. Scheme of arrangement of oxygen octahedrons in the perovskite structure (left) and the rhenium trioxide structure (right).

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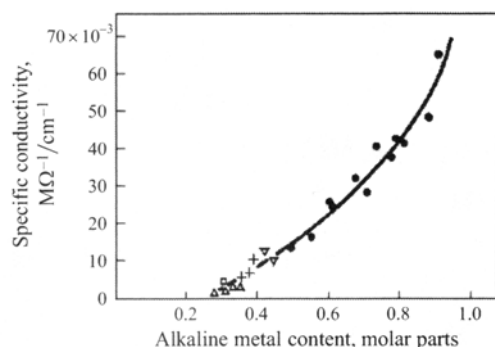
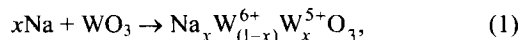
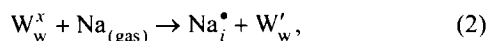


Fig. 2. Dependence of the conductivity of tungsten oxide bronze on the alkaline metal content [1]: ●) cubic bronze with sodium; ▽) tetragonal bronze with sodium; △, +) cubic bronzes with lithium; □) bronze with potassium.

the electronegativity of sodium is significantly lower than the tungsten electronegativity (0.9 against 2.0 arb. units), this creates a tendency toward the transition of the valent 3s-electron from sodium to tungsten. In that case tungsten is partly reduced:



or in the quasichemical language:



where x is zero effective charge, \cdot is positive, and $'$ is negative effective charge.

When the concentration of sodium atoms implanted in tungsten dioxide is not high, their distribution over the crystal is disordered (although statistically uniform in the case of equilibrium), and such a system can be regarded as an impurity system, i.e. as a solid solution of sodium in tungsten oxide, and its formation can be described by Eqs. (1) and (2). According to experts [1], such a system can be expected to have semiconducting properties. Indeed, experiments revealed [1] that for the values $x < 0.25$, the conductance level of Na_xWO_3 approximately corresponds to the conductance level of semiconductors (Fig. 2).

Since the arrangement of vacancies in the crystal obeys a certain law, it can be expected that an increase in the concentration of sodium atoms in the WO_3 lattice will inevitably make their arrangement finally obey the same law. In fact, Collongues [1] reported that an ordered arrangement of sodium ions was registered experimentally in studying single crystals of bronze $\text{Na}_{0.75}\text{WO}_3$.

Thus, sodium atoms, by filling respective vacancies, form their own cation sublattice. Although the concentration of sodium existing in sodium-tungsten bronze does not attain the limiting value of $x = 1$, it can be contended that the solid solution which is formed under slight concentrations of sodium in accordance with reactions (1) and (2), with an increase in the concentration of implanted sodium atoms is replaced by another chemical compound, namely, a true chemi-

cal compound, which is oxide bronze Na_xWO_3 . This transformation is accompanied by variations in the most significant parameter of these bronzes, i.e., electric conductivity, which becomes typical of metals: the level of conductance is relatively great, and its temperature coefficient is negative as in all metals.

It should be noted, however, that published data on the semiconductor conductivity of cubic sodium-tungsten bronze do not agree with each other well enough and at first glance appear contradictory [1–6]. According to Sienko, bronzes with a relatively low sodium content should have semiconductor properties. This opinion was supported by MacNeil, who registered such properties in bronze of the composition $\text{Na}_{0.363}\text{WO}_3$. However, Heig reported to have identified semiconductor properties at 20–350°C in bronze of the composition $\text{Na}_{0.78}\text{WO}_3$, and Ornatskaya did the same for bronze $\text{Na}_{0.85}\text{WO}_3$ and even $\text{Na}_{0.9}\text{WO}_3$.

However, these contradictions in all likelihood are apparent and related to the temperature at which the measurements were taken. As can be seen from experience [6], the nearest analogue of Na_xWO_3 , which is potassium-molybdenum bronze $\text{K}_{0.3}\text{MoO}_3$, at a temperature below 100°C exhibits semiconducting conductivity, and at higher temperatures has the conductivity of a metal. Presumably, a similar transformation is also typical of sodium-tungsten bronze, and it depends not only on the bronze composition but on temperature as well. The values of these two parameters determining the position of this transformation on the diagram have not yet been clearly defined. Apparently, this transformation is gradual. In any case, it is clear that as the sodium content in the bronze decreases, its conductance changes from metallic to semiconducting. It is likely that the semiconductor–metal conversion is associated with the formation of the inherent sodium sublattice. Until this sublattice is formed, the material is a semiconductor; after its formation, the material is a metal.

It is not only the type of conduction that is modified in bronze. Its optical properties are modified as well. Tungsten oxide bronze, which is rich in sodium, has the same golden-yellow tint as standard metallic bronze. However, with decreasing x_{Na} , this color changes through red and violet to bluish-violet.

The electrons acquired by tungsten atoms due to the ionization of implanted sodium in accordance with reaction (2) are not strongly fixed and at moderate temperatures close to room temperature migrate to the conductivity area. In this way, the tungsten ions, which at relative low temperatures have the oxidation degree 5+, once more resume the oxidation degree inherent in tungsten trioxide (6+):



Summing of reactions (2) and (3) gives



As can be seen from reaction (4), the concentration of free electrons should be proportional to the concentration of

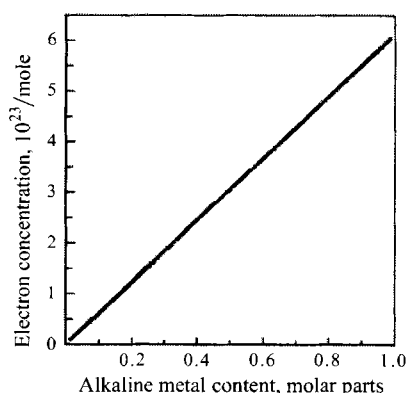


Fig. 3. Dependence of the electron concentration in tungsten oxide bronze on the sodium content.

implanted sodium. The experiment confirms this relationship [1] (Fig. 3).

Another specific feature of the oxide bronze nonstoichiometry is related to its effect on polymorphic transformations. Polymorphism is typical of sodium-tungsten bronze (Fig. 4)

At temperatures above room temperature, five separate nonstoichiometric phases can exist in a system, which are crystallized in four syngonies: cubic, two tetragonal ones (with different lattice parameters), rhombic, and a monoclinal one. There are data in the literature on the synthesis of a hexagonal modification whose boundaries are not yet identified. The cubic modification has the largest homogeneity area. Let us consider it in greater detail.

According to relationship (1), the main initial reactant forming the implantation structure is tungsten trioxide acting as a host matrix. It turns out that this compound has the same polymorphic forms, except for the cubic and monoclinal ones. According to the data in [9], these forms exist in the following temperature ranges: 20 – 339°C for the monoclinal form, 339 – 740°C for the rhombic, and 740 – 1470°C for the tetragonal one. It can be seen that as temperature increases, the degree of the crystal perfection improves. However, the most perfect, i.e., the cubic syngony, is not attained.

The correlation of these data with the information in Fig. 4 shows that by acquiring the state of an implantation structure, the host compound mostly preserves the same polymorphic forms, but they are substantially shifted to the lower temperature region.

If we follow the transformation of polymorphic forms from higher to lower temperatures, a conclusion can be drawn that filling of a crystal by the more electropositive metal increases the stability of those polymorphic forms which tend to exist at increased temperatures and are destroyed when temperature decreases. This can be clearly observed, in particular, in the tetragonal modification which is inherent both in pure oxide and in oxide enriched with sodium. This modification in oxide exists in the temperature range 740 – 1470°C but is destroyed at temperatures below

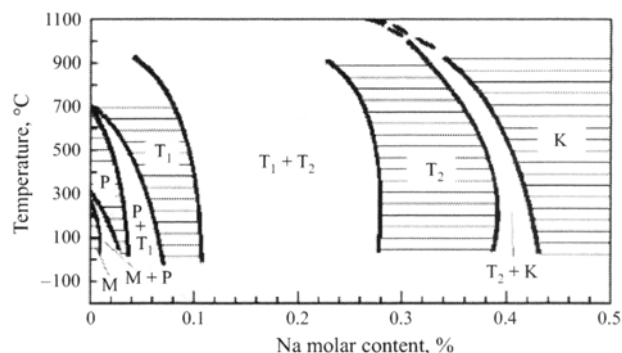


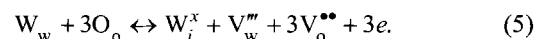
Fig. 4. A fragment of the phase diagram of sodium-oxytungsten bronze [1]. M) monoclinal; R) rhombic; T_1 , T_2) tetragonal; C) cubic (homogeneity areas are shaded).

740°C and changes over to the rhombic modification. As can be seen from Fig. 4, the introduction of around 7% sodium in oxide is sufficient for the transformation boundary to shift by nearly 700°C to a temperature close to room temperature. The same tendency is observed in other modifications as well. Moreover, in this case the phase diagram shows the highest (cubic) syngony, which cannot be attained in pure oxide.

The crystal lattice of tungsten oxide is kept together by ionic-covalent bond; therefore, the introduction of a more electropositive metal should increase the share of the ionic component and thus contribute to its greater stability. However, if the polymorphic transformation as a type of crystal-lattice rearrangement is related to mass transfer, the abundance of such transformations in tungsten oxide can be logically associated with disordering processes, since such processes should contribute to mass transfer.

Disordering, in particular, can be caused by disturbance in stoichiometry. Judging from the published data, all tungsten oxides are nonstoichiometric. According to Remy [10], tungsten trioxide tends to exist with a substantial deficit of oxygen, which can attain 5 mole % or more (according to some other data it can attain 7%). The mechanism of the origin of this deficit consists of the migration of oxygen from oxygen octahedrons in the crystal lattice, i.e., disassembly of these octahedrons.

If the polymorphic transformation is related to the mass transfer determined by nonstoichiometry, its implementation can be ensured only when both crystal components (cation and anion components) take part in mass transfer. This can be ensured, assuming that disordering evolves according to the following scheme:



In this case, the anion transfer is implemented through anion vacancies and the cation transfer through the vacancy, internodal, or relay race mechanism.

If this is so, a polymorphic transformation can be delayed, in other words, a respective polymorphic modification can be stabilized by shifting equilibrium (5) to the left. This is accomplished by introducing an electropositive (electron donor) element in the tungsten trioxide. A correlation of reactions (5) and reactions (1) – (4) shows that electrons are their unique products. Therefore, the evolution of process (4) should produce an equilibrium shift to the left in reaction (5). This will inevitably result in a decreased concentration of oxygen vacancies and excessive tungsten atoms (ions), i.e., the defects which ensure cation and anion transport and increase the resistance of the crystal to a polymorphic transformation, that is, contribute to the crystal stabilization.

If this reasoning is correct, we can expect that the content of sodium introduced in WO_3 should at least not be below the level of nonstoichiometry for this oxide. As was mentioned earlier, this level is 5 – 7%. At the same time, it can be seen from Fig. 4 that around 8% sodium should be introduced in WO_3 to delay the polymorphic transition from the tetragonal syngony to the rhombic syngony.

If all the above is correct, we can assume that the chemical nature of the more electropositive metal introduced in WO_3 is not that significant. It is essential for this metal to act as an electron donor in reactions with WO_3 . Prof. Collongues [1] noted that the bottom limit of the cubic-modification homogeneity area for sodium-tungsten oxide bronze, which is understood as the boundary of the transformation from the tetragonal modification to the cubic one, depends on the oxidation degree of the implanted atom. In implanting atoms of equal radii but different oxidation degrees, this boundary is a function of the oxidation degree of the implanted component. As the oxidation degree increases, the said boundary shifts toward lower concentrations of the implanted component. At the same time, the product of the oxidation degree and the concentration of the implanted element remains a constant value. This rule (let us call it “the Collongues rule”) can be expressed by the equation

$$\omega X_m = \text{const},$$

where ω is the oxidation degree of the implanted metal and X_m is its concentration.

The product of the oxidation degree and the concentration of the implanted element in tungsten oxide bronze for a high-temperature boundary of the transformation from tetragonal to cubic modification is given in Table 1.

TABLE 1

Implanted element	Oxidation degree ω	Atom radius, Å	Molar share of element in high-temperature transformation X_m	ωX_m
Na	1	0.97	0.25	0.25
Cd	2	0.97	0.12	0.24
Gd	3	0.97	0.085	0.25
Th	4	1.02	0.067	0.26

As can be seen, the bottom boundary of the cubic-modification homogeneity area in tungsten oxide bronze is determined by the oxidation degree of the implanted element, i.e., by the quantity of free or quasifree electrons brought in. The relationship ωX_m is essentially the concentration of free electrons in the bronze. With increasing oxidation degree of the implanted element, its minimally required concentration proportionally decreases. This minimum is a function of temperature: it is relatively low when the temperature is high, and it grows as temperature decreases.

This temperature dependence is probably due to the fact that the equilibrium is shifted in scheme (5), integrating the origination of three types of defects: anion vacancies and excessive atoms (ions) of tungsten. With increasing temperature, the disorder caused by exponentially growing removal of oxygen results in the fact that the oxygen vacancies become predominant in the overall balance of defects. According to Radgenan [11], they can also acquire the function of a stopper for diffusion processes, which can become an additional factor impeding the polymorphic transformation and thus decrease the amount of sodium introduced in WO_3 for this purpose (for high temperatures). This assumption is strongly supported in [12].

With a fixed temperature, the minimum quantity of free electrons at the interface of the cubic and tetragonal phases in any case remains constant and is a limit quantity for the crystal to preserve its cubic structure. At low temperatures this quantity is determined by the level of intracrystal disproportion of tungsten, i.e., variation in the tungsten oxidation degree from 6+ to 5+.

The same quantity of quasifree electrons which is supplied by sodium to suppress oxygen nonstoichiometry and stabilize the cubic modification of tungsten oxide bronze can be supplied by half as much cadmium, one-third as much gadolinium, and one-fourth as much thorium.

Thus, in order to prevent polymorphic transformations in WO_3 and stabilize the required crystal modification, the disordering processes caused by disturbed stoichiometry in this oxide should be suppressed or at least delayed so as to impede the mass transfer which provides for the rearrangement of the crystal lattice. In this case, we are talking of modifying spontaneous natural nonstoichiometric processes and reverting them.

Considering WO_3 in the context of synergism, i.e., the theory of self-organization of naturally evolving processes, it should be noted that the tendencies toward such development are inherent in WO_3 . They can be easily identified if we relate the conditions of origination of polymorphic transformations in WO_3 to the regularities of the evolution of nonstoichiometric phenomena.

It is seen in this case that these transformations reflect the tendency of a crystal to preserve its existence under the destructive effect of disordering caused by nonstoichiometry. As was shown in [13], this tendency in spinel is implemented via its restructuring through conversion from the normal

form to the inverted form. This phenomenon is observed in disordered WO_3 as well, although in a different form.

It is known that the stability of a polymorphic modification is determined by the level of free energy accumulated in it [1], which is related to other phase parameters and should be minimal in a stable system. Most often free energy is modified when pressure and temperature vary. The same parameters determine the nonstoichiometry level, which is expressed by the known relationship [15]

$$\varphi(P, T, X) = 0, \quad (6)$$

where X is the value of the deviation from stoichiometry, P is the pressure, and T is the temperature.

For this reason, nonstoichiometry is also regarded as a phase parameter [15]. Let us analyze its effect on polymorphic transformations in WO_3 . At high temperatures this oxide is crystallized in a tetragonal modification existing within the temperature range 740 – 1470°C. As the temperature increases, the deviation from stoichiometry in this oxide grows exponentially. According to Batsanov's estimate [16], when the level of disorder in a crystal attains a value where there is one defect (vacancy) per ten regular lattice points, the crystal is on the verge of destruction. The regularity described by Eq. (6) has not yet been studied in detail for tungsten oxide, but based on the estimates of Remy [10] and other authors, the concentration of defects due to the disturbed stoichiometry in this oxide at 1470°C can be taken equal to 7%. This means that the ability of WO_3 to preserve its tetragonal structure is nearing a limiting point, and the crystal either has to be rearranged in the more perfect cubic structure or become destroyed. It has no possibility of becoming rearranged in the cubic structure: the evaporation rate of WO_3 is substantial already at a temperature of 800°C, and with further increase in the temperature the material sublimates [9].

Let us now consider the situation in the tetragonal modification of WO_3 as it passes from the high-temperature boundary of its existence to the low-temperature boundary. If we regard the nonstoichiometric phase as a solid solution of excessive particles (or quasiparticles) in the main compound, as the temperature decreases this solution will be oversaturated. According to the thermodynamical requirements, the crystal can be said to search for a way to avoid this oversaturation and, accordingly, to get rid of some part of the enthalpy accumulated at high temperatures. The excessive ingredients either have to leave the crystal and create a new phase or associate in clusters (associates), which process is accompanied by the loss of free energy [15].

The formation of associates is determined by two conditions: first, a high concentration of elementary (non-associated) defects and, second, a low temperature [15]. If both conditions are satisfied, the formation of associates becomes inevitable. Although association of defects can be regarded

as a form of ordering, the overall level of defects in the lattice remains high. This has a simple explanation in the context of thermodynamics: if n elementary defects form an associate $(D)_n$ and under certain temperature conditions the reactions of nucleation and association of these defects are simultaneous:



then process (8) should shift the equilibrium in reaction (7) to the right.

Thus, in approaching the low-temperature boundary of the tetragonal modification, the ability of WO_3 to preserve this structure approaches its limiting point, and the crystal has to rearrange in a less perfect but thermodynamically more advantageous crystal modification, i.e., the rhombic one. The associates formed in the crystal can serve as seeds of this new structure.

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